

Fuel Cells from a Thermodynamics Perspective

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Abstract

In this essay, a Proton Exchange Membrane (PEM) type cell with pure Hydrogen as a fuel will be explored from the thermodynamic aspect. The aim of this essay is to throw light on the thermodynamics of fuel cells. First, this essay will briefly explain the workings and applications of a fuel cell system. Second, it will utilise the laws of thermodynamics for a H_2/O_2 fuel cell to explore the significance of the concepts of Gibbs free energy, the Nernst equation and irreversibilities. Third, it will delve into the influence of thermodynamic variables like pressure and temperature on fuel cell performance. Lastly, it will look at fuel cell efficiencies and compare fuel cells to Carnot engines.

Key Words: Fuel Cells, Thermodynamics, Electrochemical, PEM, Hydrogen, Gibbs Free Energy, Nernst Equation, Polarisation, Carnot Engine, Efficiency.

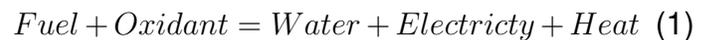
I. INTRODUCTION

A fuel cell is an energy conversion device that converts the chemical energy possessed in a fuel into electrical energy that can be used to do work (Sharaf and Orhan, 2014). Fuel cells have promising applications, not only in the transport, space and military sectors, as sources of heat and electricity, but also as energy storage and decentralised power generation systems (ibid.; Carrette et al., 2011). Fuel cell technology, in addition to catering to the increasing need for the flexible generation of electricity also proves to be a sustainable and competitive option for the co-generation of heat and electricity (ibid.).

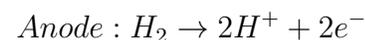
II. FUEL CELL SYSTEMS

A fuel cell is an open system, which permits the flow of mass and energy through its boundaries. It qualifies as a perfect electrochemical apparatus, which can be defined as a cell in which reversible

changes take place only on the passage of current. In a fuel cell, the general electrochemical reaction for a H_2/O_2 fuel cell that involves the transfer of electrons between electrodes, can be written as follows (DeBethune,1960):



A Proton Exchange Membrane (PEM) fuel cell (shown in figure 1) combines pure Hydrogen (H_2) and Oxygen (O_2) to produce electricity along with heat and water as by-products (depicted in 1). PEM fuel cells, once used in NASA spacecrafts, have an operating temperature of $60 - 120^\circ C$ and use a Platinum (Pt) catalyst at the electrodes with Nafion® as an electrolyte (Sharaf and Orhan, 2014; Carrette et al., 2011). The electrochemical reactions taking place at the electrodes in figure 1 are as follows (Sharaf and Orhan,2014):



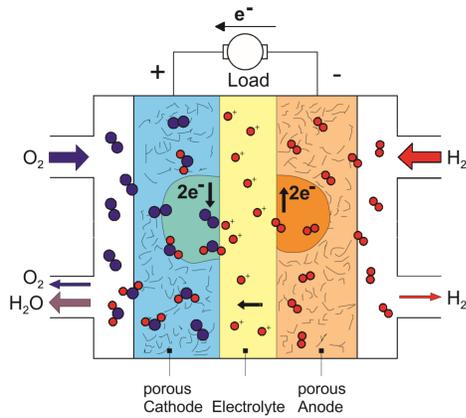


Figure 1: A H_2/O_2 PEM fuel cell (Carrette et al., 2011).

It can be identified that, since in this galvanic cell ($\Delta H = -285.8 \text{ kJ/mol}$, $\Delta G = -237.2 \text{ kJ/mol}$), the overall reaction is spontaneous and thermodynamically favoured because the free energy of the products is less than that of the reactants.

III. THERMODYNAMICS OF FUEL CELLS

The total energy of a fuel cell system can be represented as

$$\Delta H = Q - W_e \quad (2)$$

Here, H - enthalpy and Q - heat input. W_e , the amount of electrical work done by a fuel cell, can be expressed as (Larminie, 2013):

$$W_e = \text{Charge} \times \text{Voltage} = [N \times F] \times [E] \quad (3)$$

Here, N is the number of equivalents of chemical change upon which, the number of electrons transferred during the reaction, is dependent on, F is Faraday's Constant and E is the reversible cell voltage. Thus, the first law of thermodynamics for a fuel cell is

$$\Delta H = Q - N \times F \times E \quad (4)$$

However, the absence of any restriction on energy transfer and the imprecise assumption that the energy content of heat and work are equivalent, leads to the second law. The second law places a limit on the quantity of heat that can be converted into work, as it is impossible to completely convert heat absorbed by a system into work done by the system. The concept of reversibility, the quasi-static shift of

a system from an initial to final state, and entropy (S), a path independent function and a measure of the disorder in a system, are fundamental for the second law. The second law for a reversible fuel cell system can be written as

$$\Delta H = T\Delta S - N \times F \times E \quad (5)$$

i. Gibbs Free Energy

The Gibbs free energy (G) is the maximum useful work obtainable when the cell is operating reversibly and the losses are minimal. The standard free energy change of the fuel cell system can be obtained from equation (5) (Pilatowsky et al., 2011):

$$\Delta G = -nF\Delta E = \Delta H - T\Delta S \quad (6)$$

In this equation, H is a measure for the total energy of the system, S represents the "unavailable" energy due to unavoidable losses and G is the "free" energy available to do useful work.

The Gibbs free energy (G) varies with temperature and varies with the 'activity' of reactants and products which is dependent on partial pressures as shown in (7) (Larminie, 2013).

$$\Delta G = \Delta G^o - (R \cdot T) \cdot \ln \frac{P_{H_2} \times P_{O_2}^{0.5}}{P_{H_2O}} \quad (7)$$

ii. Nernst Equation

The ideal performance of a fuel cell can be represented by the Nernst equation, which portrays the relationship between the electromotive force (EMF) or non-standard reversible cell voltage (E), and the reversible standard potential (E^o), temperature (T), concentration (n) and activity. Now, if the reactants and the products are in their standard states, equation (6) can be represented as

$$\Delta G^o = -nF\Delta E^o \quad (8)$$

And since $n=2$, it can be proved that the Nernst equation for a H_2/O_2 fuel cell is (Sharaf and Orhan, 2014):

$$\Delta E = \Delta E^o + \left(\frac{R \cdot T}{2 \cdot F} \right) \cdot \ln \frac{P_{H_2} \times P_{O_2}^{0.5}}{P_{H_2O}} \quad (9)$$

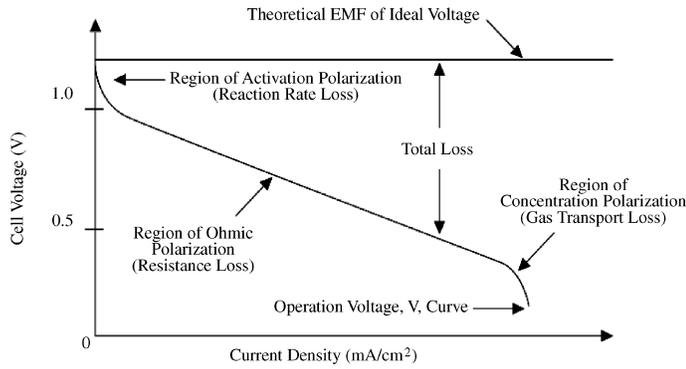


Figure 2: The ideal and actual fuel cell voltage against current density (Pilatosky et al., 2011).

iii. Irreversibilities

The reversible cell voltage (E) in (9) is only achieved if the Gibbs free energy (G) in (7) is converted, without any losses, into electrical energy. However, the actual cell voltage is lower than the reversible cell voltage due to the existence of irreversibilities (depicted in figure 2). These irreversibilities, known as cell polarisations can be represented by the polarisation equation shown in (10) (Sharaf and Orhan, 2014).

$$E = E_{rev} - E_{c,a} - E_{c,c} - E_{a,a} - E_{a,c} - E_o \quad (10)$$

The polarisation losses depicted in figure 2 consist of ohmic losses (E_o) as well as activation ($E_{a,a}, E_{a,c}$) and concentration losses ($E_{c,a}, E_{c,c}$) at the anode and cathode respectively (Pilatosky et al., 2011). It can be seen from figure 2 that the actual voltage decreases with an increase in the current density because of these irreversibilities. It should be noted that an increase in operating temperature would lead to an increase in actual voltage because of a reduction in polarisation losses as compared to a decrease in the reversible cell voltage (Sharaf and Orhan, 2014).

IV. ANALYSIS OF FUEL CELL PERFORMANCE

By analysing the change in Gibbs free energy in (6) and using the fact that $H = U + PV$, the effect of temperature and pressure on cell potential can

be examined (Pilatosky et al., 2011):

$$\left(\frac{dE}{dT}\right)_P = \frac{\Delta S}{nF} \quad (11)$$

$$\left(\frac{dE}{dP}\right)_T = \frac{\Delta V}{nF} \quad (12)$$

The following observations can be made:

- As for a reversible H_2/O_2 fuel cell $\Delta S < 0$, the cell potential (E) decreases with an increase in temperature (T) (ibid.).
- As the volume change (ΔV) is negative, cell potential increases (E) on increase in pressure (P).

V. FUEL CELL EFFICIENCIES

The amount of the total energy in a fuel cell that can be converted into usable electric work, can be expressed by the thermal efficiency. Considering the ideal condition, where the Gibbs free energy is completely converted into electrical energy, the thermal efficiency can be shown as (Carrette et al., 2011):

$$\eta_{thermal} = -\frac{W_{electric}}{\Delta H} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \quad (13)$$

The maximum achievable thermodynamic efficiency of a H_2/O_2 fuel cell at $25^\circ C$ is

$$\eta_{max} = \frac{\Delta G}{\Delta H} \times 100 = \frac{237.1}{285.8} \times 100 = 83\% \quad (14)$$

As efficiency is lowered due to the existence of polarisation losses and electrolytic resistance, the electrochemical efficiency that directly relates to fuel cell performance is considered. Now, the ideal standard or oxidation potential of a H_2/O_2 fuel cell (E°) with liquid water is 1.229 V ($\Delta G = 237.2 kJ/mol, n = 2, F = 96500 C/mole^{-1}$) (Pilatosky et al., 2011). It can be seen from (15) that the electrochemical efficiency can be improved by increasing the current density and cell voltage. Using (14)(ibid.),

$$\eta = \frac{Useful\ Work}{\frac{\Delta G}{0.83}} = \frac{EI}{\frac{E^\circ I}{0.83}} = \frac{0.83 \times E}{1.229} = 0.675E \quad (15)$$

i. Fuel cells versus Carnot heat engines

The process within a fuel cell is electrochemical as compared to a thermal process in a heat engine. As fuel cells convert chemical energy directly into electricity without first converting it into heat like combustion engines, they avoid the ‘thermal bottleneck’ or ‘Carnot Limit’ (Larmine, 2013). A heat engine that absorbs heat at a high temperature (T_1) must reject energy at a lower temperature (T_2) to do useful work. The Carnot efficiency of an ideal engine, limited by the second law, is (ibid.)

$$\eta_{carnot} = 1 - \frac{T_2}{T_1} \quad (16)$$

A maximum Carnot efficiency of 50% is reached by a steam turbine (Carrette et al., 2011). The reduced efficiencies of a Carnot Engine can be attributed to the fact that due to irreversible processes, the work output of the cell is exceeded by the energy lost in maintaining the temperature of the hot source. However, the energy lost in maintaining the temperature of the “hot source” in a fuel cell is relatively low due to its isothermal, less irreversible operation with neither temperature cycling nor a Carnot efficiency limit. To achieve the maximum fuel cell efficiency of 83%, a Carnot engine would have to operate at a high temperature (T_1) of 1753 K and a low temperature (T_2) of 298 K to achieve an equivalent efficiency. This implies that the electrochemical efficiency in equation (15) increases and the thermodynamic efficiency in (13) decreases. However, the thermal efficiency of a Carnot cycle engine increases with an increase in operating temperature as shown in figure 3. It can be noted from figure 3 that beyond a temperature of 950K (676.85°C) the H_2/O_2 fuel cell efficiency is lower than the Carnot efficiency. It can be inferred from figure 3 that a fuel cell is not a 100% efficient and that it is not limited by the Carnot limit at lower temperatures below 950K.

VI. CONCLUSION

H_2/O_2 PEM fuel cells offer great flexibility and portability due to their high modularity. They also prove to be a viable option under certain conditions with a substantially higher efficiency than traditional combustion technologies. The fact that

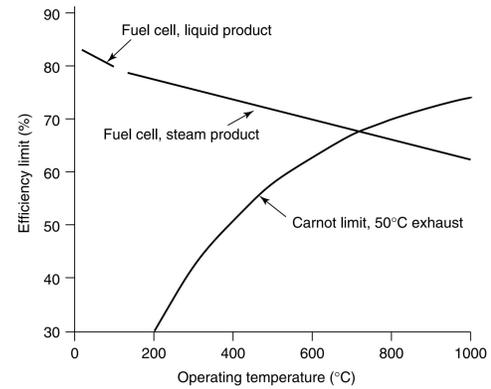


Figure 3: A graph showcasing the temperature dependence of fuel cell and Carnot efficiency (Larmine, 2013).

the waste heat energy generated can also be harnessed make fuel cells attractive in terms of cogeneration. However, they entail high costs due to expensive catalysts like Platinum (Pt) and are highly sensitive to contaminants like carbon monoxide (CO). It should be noted that, the practicality of fuel cells depends upon the resources utilized to extract hydrogen. On one hand, hydrogen could qualify as a renewable fuel, if it is produced using renewable sources of energy like wind or solar power, while on the other, it could prove to be unsustainable if non-renewable resources are used in its extraction.

VII. REFERENCES

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